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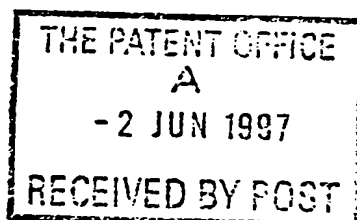
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02 JUN 1997

2. Patent application number

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3. Full name, address and postcode of the or of each applicant (underline all surnames)

ISIS INNOVATION LIMITED
2 SOUTH PARKS ROAD
OXFORD OX1 3UB

Patents ADP number (if you know it)

If the applicant is a corporate body, give the country/state of its incorporation

UNITED KINGDOM

4. Title of the invention

ORGANOMETALLIC COMPLEXES

5. Name of your agent (if you have one)

STEVENS HEWLETT & PERKINS

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Number of earlier application

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Signature Stevens Hewlett & Perkins Date 2/06/97
STEVENS HEWLETT & PERKINS

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ORGANOMETALLIC COMPLEXES

This invention relates to organometallic complexes, processes for their production, electroluminescent materials incorporating the complexes and electroluminescent devices comprising the complexes or the materials. The devices of the invention may be flat panel displays.

Flat panel displays are the critical enabling technology for many current applications, including laptop computers and "heads up" displays, as they offer several potential advantages over conventional cathode ray tube displays, including compactness and low power consumption.

Currently, the flat panel display market is dominated by liquid crystal technology, but these materials suffer several drawbacks including small operational viewing angles, poor image contrast and high power consumption. As an alternative technology for flat panel displays, electroluminescent displays using semiconducting organic polymers offer the potential of lower cost, improved viewing angles, better contrast and lower power consumption. However, these materials often have broad emission profiles, resulting in poor chromaticity and reduced device efficiency.

Typically, a flat panel device is a multilayer assembly of structurally important films consisting of a transparent electrode, insulation, phosphor and metal electrode. All are important materials in device fabrication, but the single most important element in the development of a multi-colour electroluminescent device is the phosphor.

It is known that organometallic complexes can be used as phosphors in electroluminescent devices. For example, US 5552547 describes complexes of aluminium, gallium and indium in which one of the ligands acts as a "built-in" fluorescent dye. The colour of the light which is emitted from the complex is determined by the ligand which acts as the dye.

It has been suggested that lanthanide complexes can be used as phosphors in electroluminescent devices.

M. A. Pavier et al., *Thin Solid Films*, 284-285 (1996) 644-647, describe electroluminescence from dysprosium- and neodymium- containing Langmuir-Blodgett films. The ligand used in the complexes is a pyrazolone-based molecule in which the binding to the metal by the ligand occurs via a beta-diketonate-type arrangement.

The europium complex with phenanthroline and thenoyltrifluoroacetone is disclosed in Sano et al, Jpn. J. Appl. Phys., vol.34 (1995), p. 1883-1887 and Campos et al in J. Appl. Phys., vol.80, no.12 (1996), p. 7144-7150. Both Sano et al and Campos et al teach the use of the complexes to provide red light in electroluminescent devices. Like the complexes disclosed by Pavier et al, it is the beta-diketonate part of the ligand which binds to the metal.

Campos et al mentions that fluorination of part of the beta-diketonate ligand imparts higher sensitising efficiencies to the complex. The sensitising efficiency of a complex is a measure of the

efficiency of the process of energy transfer from the ligand to the metal during the excitation step associated with electroluminescence.

Fluorination of beta-diketonate ligands in organolanthanide complexes has been proposed as a way of shielding the metal ion from quenching by water molecules when the complexes are in aqueous solution; see Meshkova et al, Sov. J. Coord. Chem., 18, 183 (1992). However, in most electroluminescent devices, metal complexes are either in the form of a thin film or are dispersed in a matrix in the substantial absence of water molecules and so quenching of the metal ion does not occur by this mechanism. Therefore, the teaching of Meshkova et al, which is based on ensuring that water molecules cannot get close to the metal, is of little relevance to organometallic complexes for use in electroluminescent devices.

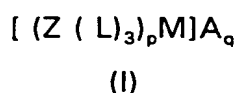
The present invention aims to provide organometallic complexes in which the metal is a lanthanide (i.e., organolanthanide complexes) which are more effective phosphors for use in electroluminescent devices than the known complexes.

The invention also seeks to provide a ligand system for organolanthanide complexes which is effective with a range of different lanthanides in order that the same ligand can provide radiation from different parts of the electromagnetic spectrum, e.g., red, green or blue light and UV or IR radiation, simply by varying the metal in the complex.

It is a further aim of the invention to improve the radiative efficiency of organolanthanide complexes. The radiative efficiency of

an organometallic complex is a measure of the amount of energy which is radiated from the complex relative to the amount of energy lost via non-radiative pathways. The known organolanthanide complexes have the problem that a number of non-radiative pathways are available for energy loss from the metal and their radiative efficiencies can therefore be relatively low.

The present invention, in one embodiment, is based on the finding that trispyrazolyl compounds are highly effective ligands for producing organolanthanide complexes useful as phosphors in electroluminescent devices. Accordingly, the invention provides an electroluminescent device comprising an organometallic complex having the formula (I):



wherein Z is a carbon atom or R¹ - B fragment

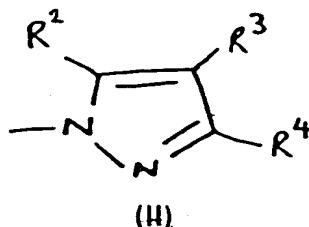
A is a monovalent anion

p is 2 or 3

q is 3 - p

R¹ is hydrogen, aryl or aralkyl each optionally substituted with from one to five halogen or C₁ to C₆ alkyl groups, C₁ to C₆ alkyl or C₁ to C₆ alkylene each optionally substituted with one or more halogen atoms

L is a group of the formula (II)



in which R^2 and R^3 are independently selected from halogen, hydrogen, aryl or aralkyl each optionally substituted with from one to five halogen or C_1 to C_6 alkyl groups, and C_1 to C_6 alkyl or C_1 to C_6 alkylene each optionally substituted with one or more halogen atoms

R^4 is hydrogen, C_1 to C_6 alkyl, C_1 to C_6 alkylene, aryl, aralkyl or $-(CX_2)_nX$ wherein n is 0 or a positive integer from 1 to 6 and X is halogen; or R^4 is orthodihalogenated or orthodiperhalomethylated aryl, optionally further substituted on the aryl ring with from one to three halogen or C_1 to C_6 alkyl groups

or either R^2 and R^3 or R^3 and R^4 are linked so as to form a fused heterocyclic ring system with the pyrazolyl ring

and M is a trivalent lanthanide metal ion.

The electroluminescent device of the invention may be a flat panel display.

The complexes of formula (I) in which R^4 is $-(CX_2)_nX$ wherein n is 0 or a positive integer from 1 to 6 and X is halogen; or R^4 is orthodihalogenated or orthodiperhalomethylated aryl, optionally further substituted on the phenyl ring with from one to three halogen or C_1 to C_6 alkyl groups are believed to be novel and are also provided by the invention.

The term "alkyl" as used herein is intended to cover branched and unbranched C₁ to C₆ groups. The term "alkylene" is defined similarly with the only difference being that the groups may contain one or more unsaturated C = C bonds.

The term "aryl" covers C₆ to C₁₀ aromatic groups such as phenyl and naphthyl. The term "aralkyl" means C₁ to C₃ alkyl substituted with aryl, such as benzyl.

The term "halogen" means fluorine, chlorine, bromine or iodine. Of these, fluorine is the preferred halogen for the complexes of the invention.

Preferably, M is terbium (Tb), cerium (Ce), europium (Eu), erbium (Er) or gadolinium (Gd). However, M may be another lanthanide metal such as praeosodymium (Pr), for example. It will be appreciated that the metal is in the M (III) oxidation state in the devices and complexes of the invention. The complexes with cerium, europium, erbium and gadolinium are preferred because they provide emissions of blue light, red light, IR radiation and UV radiation, respectively, and thus range across the electromagnetic spectrum. The complex with terbium unexpectedly gives blue light electroluminescence rather than the green light which is normally expected for terbium complexes. This is particularly advantageous since cerium complexes which are conventionally used to produce blue light have the problem of a relatively wide bandwidth for the emitted light. The terbium complexes of the present invention emit blue light with a narrower bandwidth than the previously used cerium compounds and so provide an improved alternative source of blue light for electroluminescent devices.

The trispyrazolyl ligands used in the invention have been found to be particularly effective in terms of their sensitising efficiency i.e., in transferring energy to the metal in the excitation step of the electroluminescence process. They also impart high radiative efficiencies to the complexes by providing few non-radiative pathways for relaxation (i.e., energy loss from the metal in its excited state). The ligands have been reported. Dias et al, Inorg Chem, 1995, 34, 1975 and 1996, 35, 267 and Renn et al Helv Chim Acta (1995), 78, 993 describe the synthesis of the fluorinated trispyrazolyl borate ligands. Julia et al., Organic Preparations and Procedures International, 16, 299, 1984, discloses the preparation of the trispyrazolylmethane-derived ligands.

The present invention is also based on the wider finding that non-radiative pathways for relaxation in organolanthanide complexes can be provided by carbon-hydrogen bonds in the ligand which are relatively close to the metal and the discovery that these pathways can be blocked by fluorinating the ligand to replace the carbon-hydrogen bonds by carbon-fluorine bonds or otherwise designing the ligand such that there are no carbon-hydrogen bonds within 5 Å, preferably 8 Å, more preferably 10 Å, of the metal centre (i.e., the centre of the metal atom). Therefore, in another embodiment, the invention provides electroluminescent material comprising an organometallic complex either as a film or dispersed within a matrix, the organometallic complex being a complex wherein the ligands are optionally fluorinated and arranged about the metal such that there are no carbon-hydrogen bonds within 5 Å of the metal centre.

The matrix is preferably of the type conventionally used in electroluminescent devices and based on conducting polymer systems such as polyvinylcarbazole (PVK) or polymethylmethacrylate (PMMA) with a hole transporting material such as 2-(4-biphenyl)-5-(5-tertbutylbenzene)-1,3,4-oxadiazole (BBO).

The ligands ZL_3 used in the complexes of the present invention in which R^4 is $-(CX_2)_nX$ or optionally substituted orthodihalogenated or orthodiperhalomethylated aryl are particularly advantageous for use in the electroluminescent material of the invention since they provide complexes with no carbon-hydrogen (C-H) bonds within 5 Å of the metal centre. However, it will be appreciated that other ligands can achieve the same effect and thus also block the non-radiative pathways for relaxation. It is notable that in all of the known complexes for use in matrices in electroluminescent devices mentioned above, carbon-hydrogen bonds are available for non-radiative relaxation.

The ligands used in the complexes for the electroluminescent material of the invention are preferably tridentate so that there are two or three ligands per metal atom in the complex. The term "tridentate" as used herein is intended to cover not only ligands having three atoms in different parts of the ligand molecule for binding to the metal but also three atoms sharing a delocalised electron as is the case in diamminophosphine-, benzimidine- and ketimine-based ligands, for example.

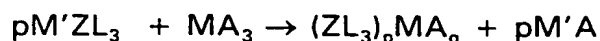
In the complexes of the invention, R^4 is conveniently trifluoromethyl. R^3 may be hydrogen and R^2 trifluoromethyl.

The counterion A in the complexes of the invention preferably should not provide non-radiative pathways for relaxation of the metal. Therefore, it is preferred that A should not contain bonds between hydrogen and other atoms, such as carbon-hydrogen bonds. Trifluoromethylsulphonate, CF_3SO_3^- , or halide (fluoride, chloride, bromide or iodide) are suitable ligands for this purpose.

In yet another embodiment, the present invention provides a process for producing the complex of the invention which comprises the steps of reacting M^{3+} ions (i.e., trivalent lanthanide ions) with ZL_3 anions in solution and separating the complex from the reaction mixture. The process is carried out in a suitable solvent at about or above room temperature up to the boiling point of the solvent for a time sufficient to form an extractable amount of the complex, preferably with stirring.

Preferably, the complex is separated from the reaction mixture by solvent extraction. To avoid the presence of water molecules in the complex which might provide non-radiative relaxation pathways, the process is preferably carried out under anhydrous conditions. It is also advantageous to exclude oxygen from the reaction mixture by carrying out the process under an inert gas atmosphere e.g., of nitrogen or argon.

The process may be carried out via the following reaction:



wherein M' is a monovalent metal such as an alkali metal e.g., sodium or potassium
and p, q, M, A, Z and L are as defined above.

In a preferred version of the process, two equivalents of $M'ZL_3$ are suspended or dissolved in a solvent and are treated with one equivalent of a trivalent lanthanide salt. The reaction mixture is stirred for a period of time between one and 100 hours either at room temperature or at a temperature up to the boiling point of the solvent under standard conditions. The solvent is removed (for example, by evaporation under reduced pressure) and the complex separated from by-products by extraction into a solvent with a different polarity from that of the reaction solvent. The product is purified by crystallisation from either the extraction solvent or a combination of solvents with different polarities.

The invention is illustrated, by way of non-limiting example only, by reference to the drawings in which:

Figure 1 shows a simplified cross-sectional view of an electroluminescent device according to the invention, such as an organic flat panel display;

Figure 2 is a current versus voltage plot for an electroluminescent device according to the invention;

Figures 3, 4 and 5 are photoluminescence plots for europium, terbium and cerium complexes of the invention; and

Figure 6 is a plot of electroluminescence intensity versus wavelength for an electroluminescent device of the invention containing a terbium complex of the invention.

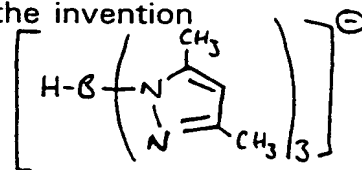
The device 10 of Figure 1 includes a substrate 1 which generally has a substantially planar surface 1a and may be a glass plate, although other suitable materials can be used for this purpose. An electrically conductive layer 2 is deposited on the planar surface 1a so as to form a relatively uniform electrical contact. Layers 3, 4 and 5 may be a single layer (for example, of the electroluminescent material of the present invention) comprising a mixture of conductive materials and luminescent dopant (such as a complex of the invention). However, it is known that this results in reduced device efficiency and a more efficient working device consists of a first organic layer 3 of a hole transporting material, the host emissive material 4 (such as the electroluminescent material of the invention), a second organic layer 5 of electron transporting material and a second electrically conductive layer 6 to form a second electrical contact.

It will be appreciated that light generated within the host emissive material 4 can be emitted either through first organic layer 3, conductive layer 2 and substrate 1 or through second organic layer 5 and second conductive layer 6. In the device 10 depicted in Figure 1, substrate 1 is formed of glass and conductive layer 2 is formed of organic and inorganic conductors, such as conductive polyaniline (PANI) or indium-tin-oxide (ITO), which are substantially transparent to visible light so that the emitted light exits downwardly through substrate 1 as the device 10 is shown in the Figure.

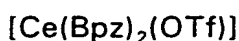
Device 10 has a potential applied between layers 2 and 6 by means of a potential source 7. In the embodiment of the invention shown in the Figure, conductive layer 2 is a p-type contact and

conductive layer 6 is an n-type contact. The negative terminal of potential source 7 is connected to conductive layer 6 and the positive terminal is connected to conductive layer 2. Electrons injected through the n-type contact are transported through organic layer 5 and into organic layer 4 (the emissive layer). Holes injected from the p-type contact are transported through the organic layer 3 and into the organic layer 4 where, upon an electron and hole recombination, a photon is emitted.

The invention will now be further described by the following examples which are not intended to limit the scope of the invention in any way. In the examples, OTf = CF_3SO_3^- and Bpz =

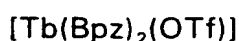


EXAMPLE 1



A mixture of $\text{Ce}(\text{OTf})_3$ (1.0g, 1.65 mmol) and KBpz (1.1g, 3.31 mmol) in THF (100 mL) were stirred at room temperature, under N_2 . The solution gradually became yellow over 1 h. The mixture was left to stir for a further 14 h and the THF was then removed under reduced pressure to give a yellow residue. The product was extracted from the yellow residue with CH_2Cl_2 (50 mL). Subsequent removal of the CH_2Cl_2 *in vacuo* afforded the product as a pale yellow solid (0.69g, 47%). A photoluminescence plot for this complex is shown in Figure 5.

EXAMPLE 2



A mixture of $\text{Tb}(\text{OTf})_3$ (1g, 1.65 mmol) and KBpz (1.1g, 3.31 mmol) in THF (100 mL) was allowed to stir for 14 h. During this

time a colourless precipitate formed. The THF was removed under reduced pressure, the colourless residue treated with CH_2Cl_2 (2 x 50 mL) and the supernatant filtered. Removal of the CH_2Cl_2 under reduced pressure gave the product as a colourless microcrystalline solid (0.87g, 58%). A photoluminescence plot for this complex is shown in Figure 4.

An electroluminescent device was prepared using this complex as a phosphor. The device had a single layer structure consisting of a homogeneous mixture of the organometallic phosphor, an electron carrying material and a hole carrying material. This layer was deposited by spin-coating a stock solution of these materials onto an indium-tin oxide coated glass substrate in a dry nitrogen atmosphere. The stock solution was prepared in a dry nitrogen atmosphere using a mixture of the organometallic phosphor, polyvinylcarbazole (PVK) and 2-(4-biphenyl)-5-(5-tertbutylbenzene)-1,3,4-oxadiazole (BBO). This solid mixture was then dissolved in THF to give a solution having the following concentrations: $[\text{Tb}(\text{Bpz})_2(\text{OTf})]$, 4.0 gdm^{-3} ; PVK, 20.0 gdm^{-3} ; BBO, 20.0 gdm^{-3} . The counter electrode consisted of a magnesium contact overcoated with aluminium. A current versus voltage plot for the device is shown in Figure 2 and an electroluminescence intensity versus wavelength plot is shown in Figure 6.

EXAMPLE 3

$[\text{Eu}(\text{Bpz})_2(\text{OTf})]$

A mixture of $\text{Eu}(\text{OTf})_3$ (1g, 1.67 mmol) and KBpz (1.11g, 3.30 mmol) was suspended in THF (100 mL) and the mixture stirred at room temperature for 12 h. A fine pale precipitate formed after 1 h and the solution became pale yellow in colour. The THF was removed *in vacuo* and the product was extracted from the resulting pale yellow solid with CH_2Cl_2 (2 x 50 mL). Evaporation of the CH_2Cl_2 under reduced pressure gave the product as a pale yellow powder (1.16g, 78%). A photoluminescence plot for this complex is shown in Figure 3.

EXAMPLE 4

$[\text{Er}(\text{Bpz})_2(\text{OTf})]$

$\text{Er}(\text{OTf})_3$ (2g, 3.25 mmol) and KBpz (2.19g, 6.51 mmol) were mixed together under N_2 and THF (100 mL) was added. A fine colourless precipitate formed during the first 1 h of the reaction, whilst the solution remained a pale pink colour. This mixture was left to stir for 12 h overnight and then the THF was removed under reduced pressure. The pale pink product was extracted from the residue with CH_2Cl_2 (2 x 50 mL) and isolated as a powder by evaporation of the solution under reduced pressure (2.46g, 83%).

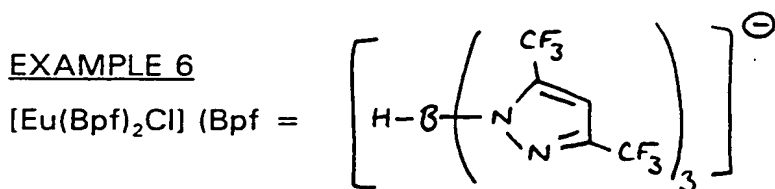
EXAMPLE 5

$[\text{Eu}(\text{Bpz})_2(\text{Cl})]$

EuCl_3 (1g, 3.87 mmol) and KBpz (2.6g, 7.82 mmol) were mixed together under N_2 and THF (100 mL) was added. The resulting mixture was stirred for 1 h, by which time the solution had changed colour to orange and a fine colourless precipitate had formed. This mixture was left to stir for 14 h and then the THF was removed *in vacuo*. The product was extracted from the resulting pale yellow

solid with CH_2Cl_2 (2 x 50 mL) and the resulting solution was then evaporated to dryness giving a pale yellow powder. This powder was washed with hexane (50 mL) and recrystallised from hot toluene to give the product as a yellow solid (0.48g). A second crop of crystals (0.87g) was obtained by concentrating the toluene supernatant (1.35g, 45%).

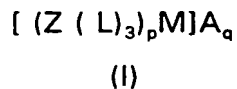
EXAMPLE 6



$\text{Eu}(\text{OTf})_3$ (0.257 g, 0.43 mmol) and $\text{KBpf}(\text{DMAC})$ (0.64 g, 0.86 mmol) were mixed under nitrogen and THF (100 mL) was added dropwise to the mixture at room temperature. After 26 hours, the THF was removed by vacuum and the product extracted from the resulting orange oil with THF (100 mL). The product was recovered from the THF solution as a pale brown solid by precipitation after concentration of the solution to 10 mL followed by addition of a large volume of hexanes (500 mL). The solid was dried under dynamic vacuum at room temperature for 4 hours. Yield: 0.36 g (54%).

CLAIMS

1. Electroluminescent device comprising an organometallic complex having the formula (I):



wherein Z is a carbon atom or R¹ - B fragment

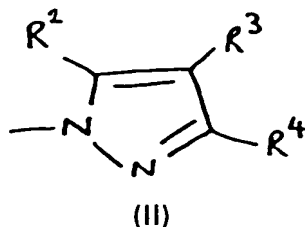
A is a monovalent anion

p is 2 or 3

q is 3 - p

R¹ is hydrogen, aryl or aralkyl each optionally substituted with from one to five halogen or C₁ to C₆ alkyl groups, C₁ to C₆ alkyl or C₁ to C₆ alkylene each optionally substituted with one or more halogen atoms

L is a group of the formula (II)



in which R² and R³ are independently selected from halogen, hydrogen, aryl or aralkyl each optionally substituted with from one to five halogen or C₁ to C₆ alkyl groups, and C₁ to C₆ alkyl or C₁ to C₆ alkylene each optionally substituted with one or more halogen atoms

R^4 is hydrogen, C_1 to C_6 alkyl, C_1 to C_6 alkylene, aryl, aralkyl or $-(CX_2)_nX$ wherein n is 0 or a positive integer from 1 to 6 and X is halogen; or R^4 is orthodihalogenated or orthodiperhalomethylated aryl, optionally further substituted on the aryl ring with from one to three halogen or C_1 to C_6 alkyl groups

or either R^2 and R^3 or R^3 and R^4 are linked so as to form a fused heterocyclic ring system with the pyrazolyl ring

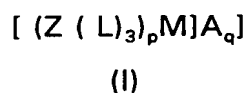
and M is a trivalent lanthanide metal ion.

2. Device as claimed in claim 1, wherein M is Tb, Ce, Eu, Er or Gd.
3. Device as claimed in claim 1 or claim 2, wherein R^4 is $-(CX_2)_nX$ or orthohalogenated or orthodiperhalomethylated aryl.
4. Device as claimed in claim 3, wherein R^4 is trifluoromethyl.
5. Device as claimed in any one of claims 1 to 4, wherein R^3 is hydrogen and R^2 is trifluoromethyl.
6. Device as claimed in any one of claims 1 to 5, wherein Z is H-B.
7. Device as claimed in any one of claims 1 to 5, wherein Z is a carbon atom.

8. Device as claimed in any one of claims 1 to 7, wherein A is CF_3SO_3 or a halide ion.

9. Device as claimed in any one of claims 1 to 8 which is a flat panel display.

10. Organometallic complex having the formula (I)



wherein Z, A, p, q, R^1 , R^2 , R^3 , L and H are as defined in claim 1 and R^4 is $-(\text{CX}_2)_n\text{X}$ wherein n is 0 or a positive integer from 1 to 6 and X is halogen; or R^4 is orthodihalogenated or orthodiperhalomethylated aryl, optionally further substituted on the aryl ring with from one to three halogen or C_1 to C_6 alkyl groups

11. Complex as claimed in claim 1, wherein M is Tb, Ce, Eu, Er or Gd.

12. Complex as claimed in claim 10 or claim 11, wherein R^4 is trifluoromethyl.

13. Complex as claimed in any one of claims 10 to 12, wherein R^3 is hydrogen and R^2 is trifluoromethyl.

14. Complex as claimed in any one of claims 10 to 13, wherein Z is H-B.

15. Complex as claimed in any one of claims 10 to 13, wherein Z is a carbon atom.

16. Complex as claimed in any one of claims 10 to 15, wherein A is CF_3SO_3 or a halide ion.

17. Process for producing the complex of any one of claims 10 to 16 comprising the steps of reacting M^{3+} ions with ZL_3^- ions in solution and separating the complex from the reaction mixture.

18. Process as claimed in claim 17, wherein the complex is separated from the reaction mixture by solvent extraction.

19. Process as claimed in claim 17 or claim 18 which is carried out under substantially anhydrous conditions.

20. Electroluminescent material comprising an organometallic complex either as a film or dispersed within a matrix, the organometallic complex being a complex of a trivalent lanthanide metal with from 1 to 3 ligands wherein the ligands are optionally fluorinated and are arranged about the metal such that there are no carbon-hydrogen bonds within 5\AA of the metal centre.

21. Electroluminescent material as claimed in claim 20, wherein the ligands are tridentate and there are two ligands per metal ion in the complex.

22. Electroluminescent material as claimed in claim 20 or claim 21, wherein the complex is a complex of any one of claims 10 to 16.

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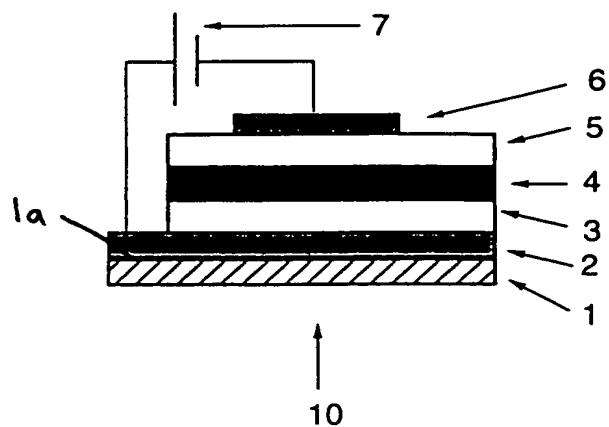


FIG. 1

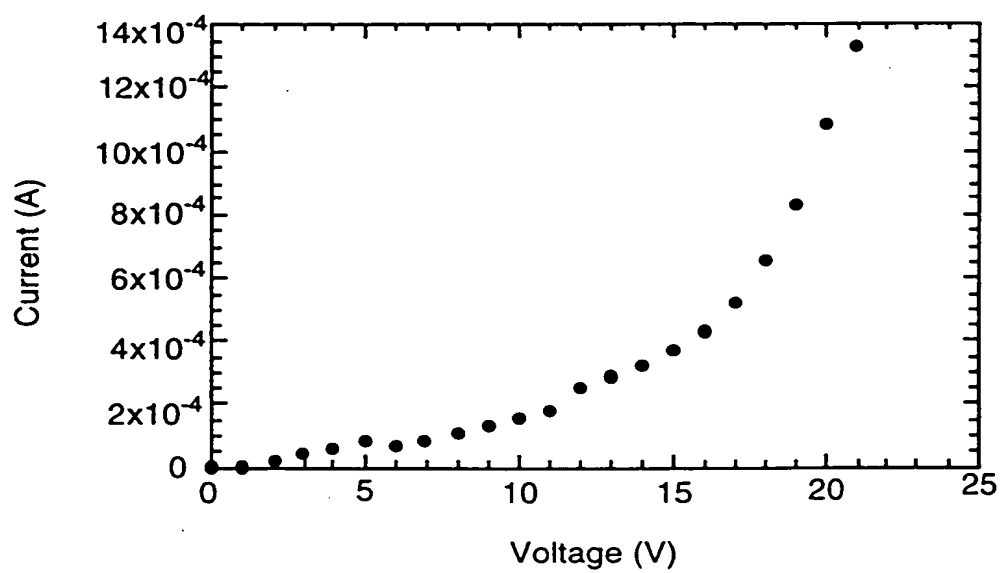


FIG. 2

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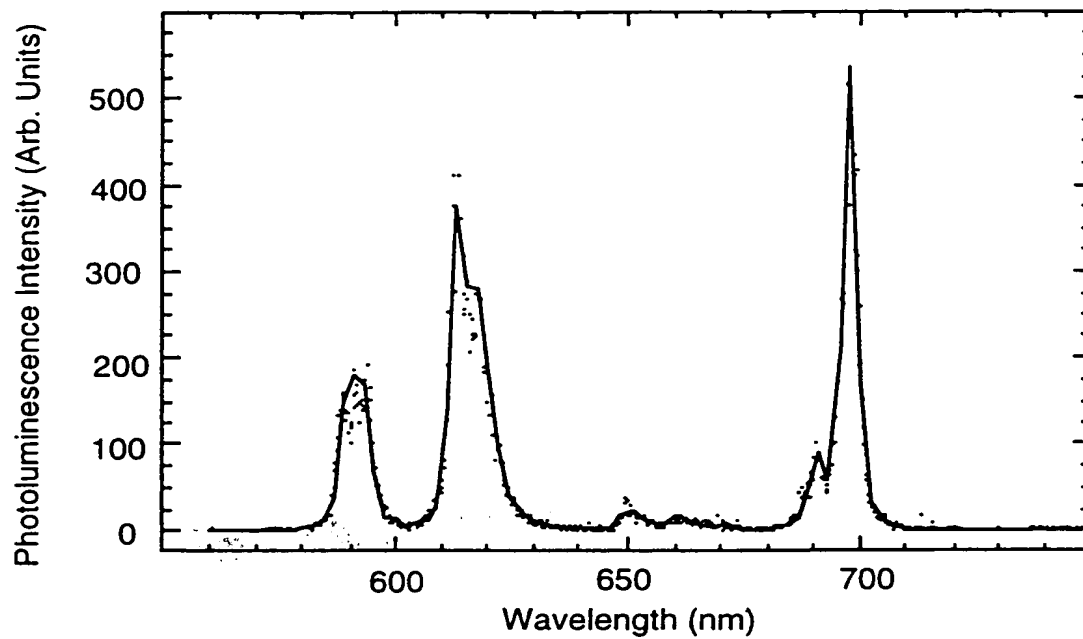


FIG. 3

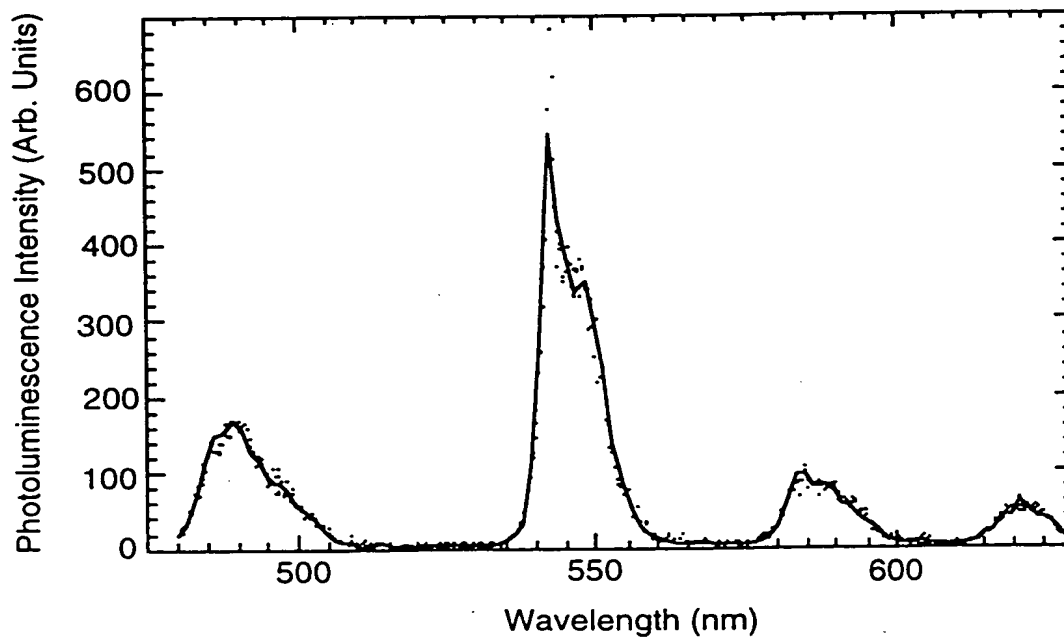


FIG. 4

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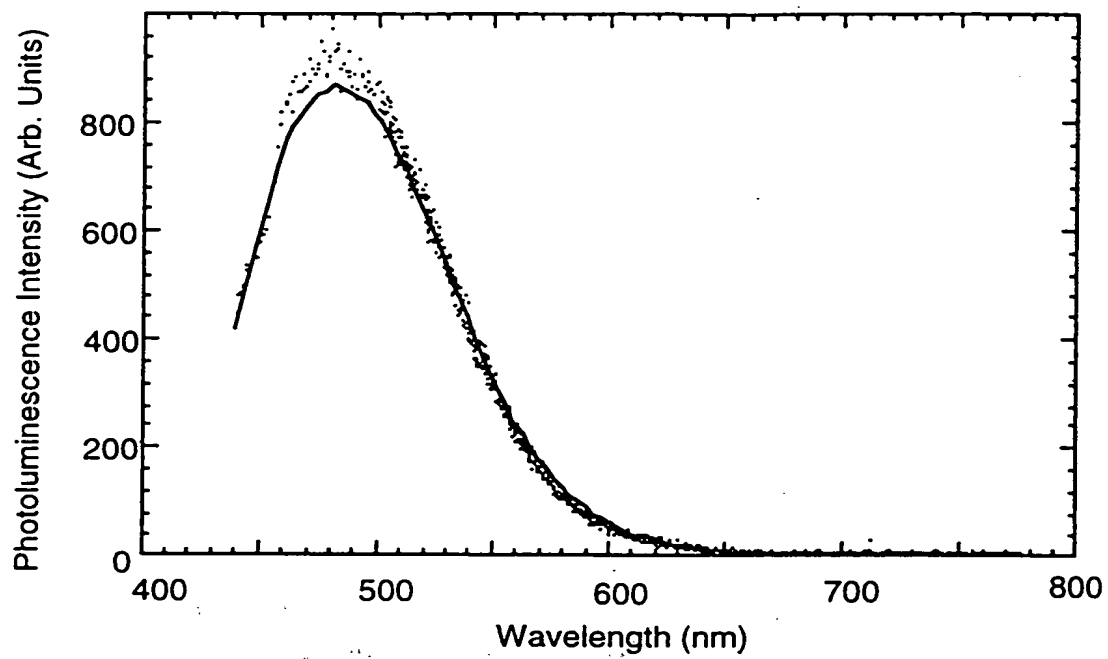


FIG. 5

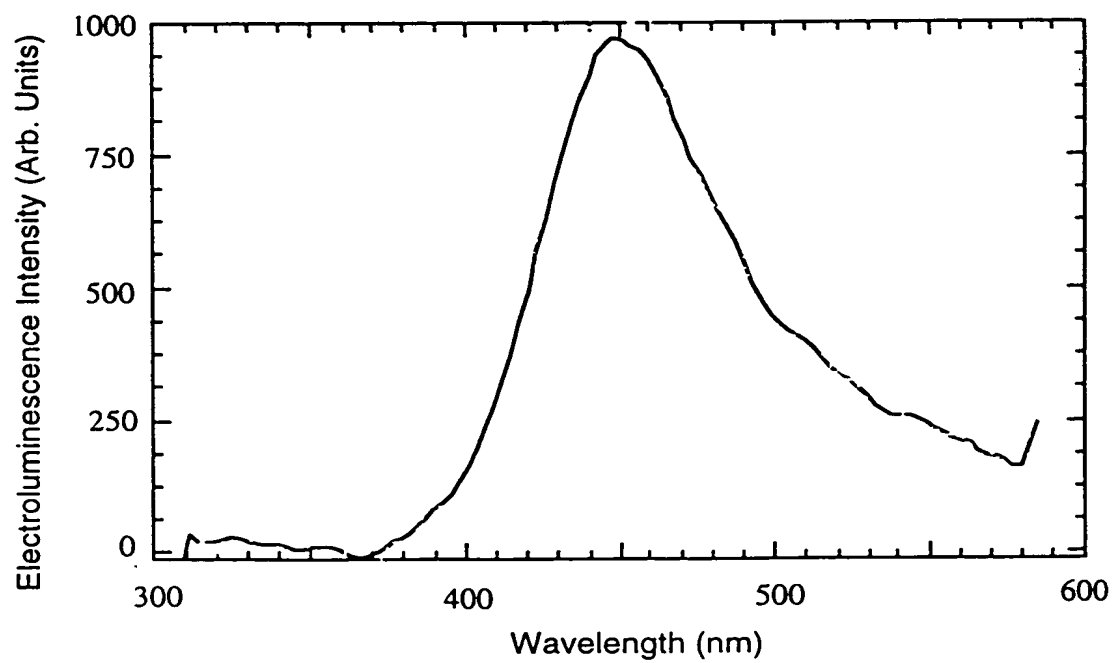


FIG. 6

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